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INFRARED REFLECTANCE AND EMITTANCE OF SILVER AND GOLD EVAPORATED IN ULTRAHIGH VACUUM

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ABSTRACT. The reflectance of silver and gold evaporated in ultrahigh vacuum has been measured in the wavelength range from 0.5 μ to 32 μ. It was found that the reflectance of both materials is higher than previously reported values, and that ultrahigh vacuum silver films have the highest infrared reflectance over an extended wavelength range of any known material. The infrared emittance of uhv gold films is nearly as low as that of silver and is smaller by nearly a factor of 3 than the value previously reported for this material. Since gold is chemically inert and its emittance apparently does not change with time, it should find wider application as a low infrared emittance material, particularly in problems involving radiative heat transfer.

U.S. NAVAL ORDNANCE TEST STATION

China Lake, California

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FOREWORD

This report discusses the reflectance and emittance of silver and gold films evaporated in ultrahigh vacuum. The measurements were made with high precision at normal incidence in the 0.5 to 32 μ wavelength region. Both materials have a higher reflectance than has previously been reported and ultrahigh vacuum silver films have the highest infrared reflectance over an extended wavelength range of any known material.

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Infrared Reflectance and Emittance of Silver and Gold Evaporated in Ultrahigh Vacuum

Jean M. Bennett and E. J. Ashley

The reflectance of silver and gold evaporated in ultrahigh vacuum has been measured in the wavelength range from 0.5 μ to 32 μ. It was found that the reflectance of both materials is higher than previously reported values, and that ultrahigh vacuum silver films have the highest infrared reflectance over an extended wavelength range of any known material. The infrared emittance of uhv gold films is nearly as low as that of silver and is smaller by nearly a factor of 3 than the value previously reported for this material. Since gold is chemically inert and its emittance apparently does not change with time, it should find wider application as a low infrared emittance material, particularly in problems involving radiative heat transfer.

Introduction

In optical systems containing many mirrors, it is desirable to have the reflectance of the mirrors as high as possible to minimize energy losses in the system. For example, if there are ten reflections and each mirror has a reflectance of 0.90, then 0.35 of the initial energy is transmitted by the system. However, if the reflectance of each mirror is increased to 0.95, the same system will transmit 0.60 of the incident energy. A second reason for interest in high infrared reflectance materials is that such materials have a low infrared emittance. In infrared optical systems where the radiation is chopped, it is necessary to have the emittance of the chopper as low as possible in order to minimize spurious signals arising from chopper radiation. At room temperature the peak of the blackbody curve lies near 10 μ, so that most of the radiation from the chopper will be in the 10 μ to 30 μ wavelength range. A material with a low infrared emittance is also important in radiative heat transfer problems. In order to minimize either radiant heating or heat loss by radiation, it is necessary to keep the emittance as low as possible over the wavelength region where appreciable thermal radiation can occur. Unless the material is at a high temperature, it radiates appreciably only in the infrared, so that by keeping the infrared emittance low, radiative heat loss can be minimized. For example, in cryostats nearly all the heat transfer is by radiation, so that it is very important that the surfaces of the cryostat have a low infrared emittance. Another example is the problem of maintaining approximately room temperature inside orbiting satellites to permit proper functioning of electronic components and other associated equipment. This temperature control is dependent on the emittance of the coating on the surface of the satellite.

Evaporated aluminum films have been widely used as high-reflectance, low-emittance coatings. However, aluminum has a minimum in its reflectance curve in the near infrared, making it less desirable as a mirror coating in systems used in the near infrared at wavelengths shorter than 3 μ. Both silver and gold have higher reflectances than aluminum in the near infrared, and also have lower emittances at longer wavelengths. Gold seems to be the most promising of the two materials because, in contrast to silver, it does not tarnish and keeps its high reflectance indefinitely.

In a previous investigation of the properties of aluminum evaporated in ultrahigh vacuum,[1] it was found that the infrared reflectance was higher than that of aluminum evaporated in a conventional system. There are theoretical reasons for supposing that the infrared reflectance of silver and gold as well should be higher than the previously reported values. The theoretical infrared reflectance of both silver and gold may be calculated from the relaxation time of the conduction electrons and the dc conductivity.[1] The calculated values of the infrared reflectance are higher than the reported values by about 1% for gold and 0.7% for silver. Hence it was decided to investigate the optical properties of silver and gold evaporated in ultrahigh vacuum.

Experimental

In order to prepare films of silver and gold with reproducible properties, the cleaning procedure and

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evaporation conditions are very important. The cleaning procedure was that usually used for all work in this laboratory.[2] The 3.8-cm diam supersmooth fused quartz optical flats were first rinsed with a concentrated sodium hydroxide solution, then with dilute nitric acid, and finally with Alconox, a detergent. The flats were then rinsed with distilled water and were washed for about 15 min in an ultrasonic cleaner filled with a solution of distilled water and Alconox. After a second rinse in distilled water, the flats were rinsed for about 15 min in a Weir washer where continuously repurified conductivity water was circulated over the flats. The flats were dried on edge under vacuum and were not touched from the time they were placed in the ultrasonic cleaner until they were completely dry, and were then handled only with rubber gloves or fingercots. Sodium hydroxide slowly etches the surfaces of the optical flats, so that after a year or so they have to be repolished. In all the experiments, care was taken to use only optical flats whose surfaces were in good condition. Of course, for infrared measurements the surface roughness requirements are considerably less stringent than for visible or ultraviolet measurements.[2]

The evaporation was performed in a Varian ultrahigh vacuum system* which incorporates a 400 l/sec ion pump with three sorption pumps. The system is thus entirely free of oil vapor from diffusion or fore pumps. After a 6-h bakeout at 250°C, a pressure of 5×10^{-10} torr could be obtained. The silver, of 99.999+% purity,† was placed in a tantalum boat made from 0.13 mm tantalum sheet and was first outgassed and melted down in a vacuum of 10^{-4} torr. The boat and its contents were then transferred to the ultrahigh vacuum system which was baked out to obtain a pressure of 5×10^{-10} torr. When the silver was remelted in ultrahigh vacuum, the pressure rose initially to about 5×10^{-6} torr but then dropped immediately to about 2×10^{-9} torr. At this time the shutter was opened, and the silver evaporated onto substrates 58.4 cm away from the source. An opaque coat was formed in about 30 sec, so that the evaporation rate was about 50 Å/sec.

The evaporation procedure for gold was similar to that used for silver, except that the boat was made from 0.25-mm molybdenum sheet. Although silver can be evaporated from either tantalum or molybdenum boats, gold alloys with tantalum very rapidly, making it unusable as a boat material. Gold alloys with molybdenum at a much slower rate, so that an opaque gold coating can be produced before the boat is destroyed. Gold of 99.999+% purity‡ was used and, as with the silver, was first outgassed in a 10^{-4} torr vacuum system. In the ultrahigh vacuum system the pressure during evaporation was 5×10^{-9} torr, and an opaque coat was produced in approximately 60 sec. The evaporation rate was approximately 30 Å/sec with a heater current of 200 A. It was found that, if a 12.7 cm coating distance was used rather than the 58.4-cm coating distance, the gold films had a lower reflectance. This reflectance decrease was 3% at 0.5 μ and 1% at 1 μ. The reason for the lower reflectance is not known.

After the evaporation was completed, dry nitrogen was admitted to the vacuum system to return it to atmospheric pressure, and the films were transferred to the reflectometer where they remained in an atmosphere of dry nitrogen during all the measurements. The NOTS absolute reflectometer, which has been described previously,[3] was used for all the measurements. Most systematic errors normally present in reflectance measurements have been eliminated in this instrument. For example, the effect of sample tilt has been cancelled optically. The contribution of scattered light is negligible; at 32 μ, the longest wavelength used, it is less than 0.05% of the observed signal. The average angle of incidence on the sample is about 5° so that, within the precision of the measurements, the measured reflectance is equal to the reflectance at normal incidence. The average deviation of the measured reflectance values from a smooth curve is about ±0.04%, and the accuracy of the measurements is about ±0.1%.

Results

The reflectance of several ultrahigh vacuum silver and gold films was measured, and the average values of both the reflectance and emittance for silver are listed in Table I for the wavelength region from 0.4 μ to 32 μ. The values for gold are given in Table II for the 0.575–32 μ wavelength region. For both materials, samples from different evaporations had reflectances which agreed within 0.1% in the wavelength regions for which data are given. At shorter wavelengths, both materials have minima in their reflectance spectra

Table I. Reflectance and Emittance of Ultrahigh Vacuum Silver Films

$\lambda(\mu)$	R	ϵ	$\lambda(\mu)$	R	ϵ
0.400	0.9564	0.0436	7	0.9950	0.0050
0.450	0.9706	0.0294	8	0.9951	0.0049
0.500	0.9786	0.0214	9	0.9952	0.0048
0.550	0.9831	0.0169	10	0.9953	0.0047
0.600	0.9860	0.0140	11	0.9954	0.0046
0.650	0.9880	0.0120	12	0.9954	0.0046
0.700	0.9894	0.0106	13	0.9955	0.0045
0.800	0.9916	0.0084	14	0.9955	0.0045
0.900	0.9929	0.0071	16	0.9956	0.0044
1.000	0.9936	0.0064	18	0.9956	0.0044
1.200	0.9938	0.0062	20	0.9956	0.0044
1.500	0.9939	0.0061	22	0.9956	0.0044
2.000	0.9940	0.0060	24	0.9957	0.0043
3.000	0.9942	0.0058	26	0.9957	0.0043
4.000	0.9944	0.0056	28	0.9958	0.0042
5.000	0.9946	0.0054	30	0.9958	0.0042
6.000	0.9948	0.0052	32	0.9958	0.0042

* Model 935-0006 obtained from Varian Associates, Palo Alto, Calif.

† Obtained from Johnson, Matthey and Company, Ltd., London, England.

‡ Obtained from American Smelting and Refining Company, Central Research Laboratories, South Plainfield, N.J.

Table II. Reflectance and Emittance of Ultrahigh Vacuum Gold Films

λ(μ)	R	ε	λ(μ)	R	ε
0.575	0.8708	0.1292	9	0.9939	0.0061
0.600	0.9116	0.0884	10	0.9939	0.0061
0.650	0.9566	0.0434	11	0.9940	0.0060
0.700	0.9695	0.0305	12	0.9940	0.0060
0.800	0.9795	0.0205	13	0.9940	0.0060
0.900	0.9839	0.0161	14	0.9940	0.0060
1.000	0.9860	0.0140	16	0.9940	0.0060
1.200	0.9878	0.0122	18	0.9940	0.0060
1.500	0.9896	0.0104	20	0.9940	0.0060
2.000	0.9914	0.0086	22	0.9941	0.0059
3.000	0.9930	0.0070	24	0.9941	0.0059
4.000	0.9938	0.0062	26	0.9941	0.0059
5.000	0.9938	0.0062	28	0.9941	0.0059
6.000	0.9939	0.0061	30	0.9942	0.0058
7.000	0.9939	0.0061	32	0.9942	0.0058
8.000	0.9939	0.0061			

because of interband transitions. The magnitude of the reflectance and the sharpness of the 3100-Å minimum in silver varied from sample to sample but the wavelength position did not change. For gold a similar situation occurred. There is a sharp primary minimum at 2350 Å and several broader and shallower minima at longer wavelengths. The reflectances of all these minima varied from sample to sample but the wavelength positions did not change.

In Fig. 1 the infrared reflectance of uhv silver and gold is plotted vs wavelength. The reflectance of uhv aluminum[1] is also given for comparison. It is seen that both uhv silver and gold have a higher reflectance than uhv aluminum in the 0.6–32 μ wavelength region. In the near infrared, this increase in reflectance is particularly large. The reflectance of uhv silver is over 0.99 for wavelengths longer than 0.75 μ, and, in fact, uhv silver has the highest infrared reflectance over an extended wavelength region of any known material. It is approximately 0.006 higher than the values reported for silver films freshly evaporated in a standard vacuum system.[4] The reflectance of uhv gold is also over 0.99 for wavelengths longer than 1.6 μ, and is higher than the previously reported values for evaporated gold films by as much as 0.01.[4] The reflectance of uhv aluminum, on the other hand, does not even reach 0.99 until the wavelength becomes longer than 20 μ, and, in the 0.6–2.5 μ region, the reflectance is under 0.98. Hence, both uhv silver and gold have a higher infrared reflectance than uhv aluminum, particularly in the near infrared in the region of the reflectance minimum of aluminum.

The infrared emittance of both uhv silver and gold is clearly less than that of uhv aluminum. At 10 μ, where the peak of the blackbody curve for room temperature radiation occurs, the emittance of uhv gold is half that of uhv aluminum, whereas the emittance of uhv silver is even less. It is interesting to note that the reported emittance at 10 μ for gold freshly evaporated in a standard vacuum system is 0.016,[4] whereas the value obtained for uhv gold is 0.006, an improvement by nearly a factor of 3. Hence uhv gold and also uhv silver appear to be excellent low-emittance materials for applications involving radiative heat transfer.

In order to separate the effect of the ultrahigh vacuum on the reflectance of silver and gold from possible differences caused by cleaning procedure, smoothness of substrates, purity of material, evaporation rate, evaporation distance, etc., evaporations were also made in a vacuum of 1×10^{-5} torr keeping the other parameters nearly constant. At 10 μ the reflectance of silver was lower by about 0.00[illegible] and the difference increased with decreasing wavelength. It was also found that the reflectance of silver evaporated at $1 \times$ [illegible]$^{-5}$ torr was not as reproducible as that of uhv silver. It was not possible to evaporate gold at 1×10^{-5} torr using a molybdenum boat, since the boat was destroyed before a sufficiently thick coating of gold could be produced. However, gold films produced using an electron gun source and evaporation rates comparable to those for the uhv films had reflectances which were approximately 0.003 lower than uhv gold at 10 μ, and the difference increased with decreasing wavelength. It was more difficult to prepare gold films with reproducible reflectances in a vacuum of 1×10^{-5} torr than it was to prepare silver films. However, even in the case of silver films, the reproducibility of the reflectance depended strongly on the evaporation conditions. For example, one silver film deposited in a very rapid evaporation at 1×10^{-5} torr using an electron gun source had a reflectance equal to that of uhv silver for wavelengths longer than 4 μ.

A supposed problem with using evaporated gold films is that a considerable film thickness is required for an opaque coating in the visible. The filament of a tungsten lamp can just barely be seen through a 2200-A gold film; the transmittance of this film is 0.0001 at 0.5 μ. However, since for most applications an opaque film is desired only for use in the infrared, it need be only about half as thick. A 1200-Å thick gold film transmits 0.0001 of the incident light at 1 μ. Hence, for infrared mirrors or low emittance coatings, the film does not need to be opaque in the visible; the 1200-A gold film transmits 0.01 at 0.5 μ.

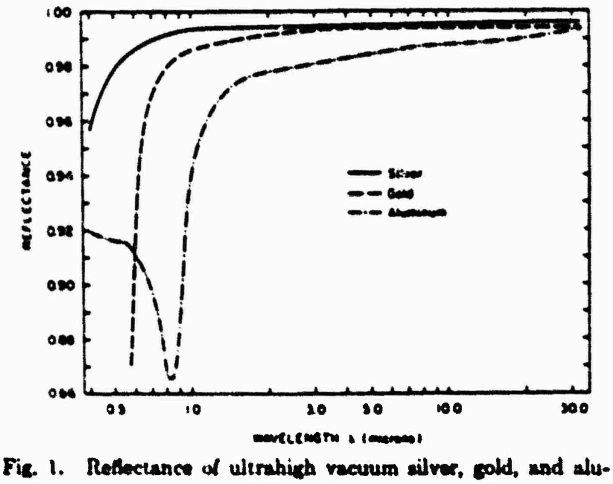

Fig. 1. Reflectance of ultrahigh vacuum silver, gold, and aluminum films.

The high infrared reflectance and low emittance of uhv silver and gold films make them ideal optical materials if the problems of adherence, mechanical stability, and aging can be solved. Freshly evaporated films of both silver and gold are soft and can be easily scratched, and stripped from the substrate with collodion or Scotch tape.[5] Fortunately, in time the films harden and become more adherent. Gold films in particular are difficult to strip after a period of a week or so. In order to remove aged gold films from optical flats, a solution of potassium cyanide must be used.[6] Of course, care should be taken to keep acids away from the potassium cyanide so that hydrogen cyanide will not be formed. Silver can be easily removed with dilute nitric acid until the layer of silver sulfide becomes thick enough to prevent the acid from reaching the underlying silver layer.

Besides letting the silver and gold films harden for a period of time, a second method of improving the adherence is to subject the substrates to a short ac or dc glow discharge prior to the evaporation.[7] The reason for this effect is not well understood, for although it is clear that the discharge removes adsorbed gas from the surface,[8] there is also the possibility of sputtering metal or metal oxide from the electrode onto the substrates, or coating them with a residue from the pump oil.[9] In this laboratory it was found that the films did, indeed, adhere better when the substrates were given a short dc glow discharge prior to the evaporation. Since aluminum has the lowest sputtering rate of any of the common metals,[10] an aluminum ball was used as the anode, and a glass shield limited the discharge to the immediate area around the substrates. It was found that when this discharge was continued for an extended period, a greyish film formed on the flats which was not removed by dilute nitric acid but which came off easily with a solution of sodium hydroxide. It, thus, appears that this material was aluminum sputtered from the aluminum anode or the aluminum substrate holder. For this reason, no glow discharge was used for the uhv evaporations.

The problem of a reflectance decrease during aging occurs only with silver. During the aging of silver in air, a layer of silver sulfide forms on the surface causing the reflectance to drop. This tarnishing may be prevented by coating the silver with a thin protective layer of a transparent material, such as calcium fluoride or quartz.[11] Alternately, if uncoated silver is stored in an atmosphere of dry nitrogen, it will retain its high reflectance for long periods. It was found that the reflectance of one uhv silver film stored in dry nitrogen dropped by less than 0.1% in the wavelength region from 0.7 μ to 32 μ over a period of 42 days. The reflectance of this film dropped by 2.2% at 4000 Å in the same period. Silver films prepared in a conventional vacuum system sometimes but not always tarnish when stored in an atmosphere of dry nitrogen. One film retained its initial infrared reflectance for a period of over a week, but there have been other films, particularly ones which are not opaque, whose reflectance has dropped by several percent the first day after evaporation even when they were stored in dry nitrogen. Hence, it is thought that the optical properties of uhv silver are more reproducible than those of silver prepared in vacuums of 10^{-4} torr, where the particular contaminants in the vacuum system may be of prime importance.

The problem of a reflectance decrease during aging does not occur with uhv gold. The reflectance of one gold film changed by less than 0.1% in the wavelength region from 0.575 μ to 32 μ over a period of 4 months. During this period the film was stored at different times in air, dry nitrogen, and under a forepump vacuum. Hence, gold appears to be an excellent material for infrared mirrors and low-emittance coatings.

Conclusions

The infrared reflectance of both silver and gold evaporated in ultrahigh vacuum is significantly higher than that previously reported for those materials, and uhv silver films have the highest infrared reflectance over an extended wavelength region of any known material. Both materials have a higher infrared reflectance and lower infrared emittance than uhv aluminum for wavelengths longer than 0.6 μ. The infrared emittance of both uhv silver and gold is also lower than the previously reported values for these materials. At 10 μ, the emittance of uhv gold is lower by nearly a factor of 3 than the previous value for gold, and the emittance of uhv silver is less than that of uhv gold. It has been found that the infrared reflectance of uhv gold does not change over long periods of time, and that uhv silver will also retain its high reflectance if stored in an atmosphere of dry nitrogen. Hence, uhv gold in particular should make an excellent mirror material in the near infrared in the region where the reflectance of aluminum drops to its minimum value. Furthermore, uhv gold should also find wide application as a low emittance material in problems involving radiative heat transfer.

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